

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 381 870 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **12.05.93** (51) Int. Cl.⁵: **C10G 11/18**

(21) Application number: **89200285.8**

(22) Date of filing: **08.02.89**

Divisional application 92200692.9 filed on
08/02/89.

(54) **Process for the production of olefins.**

(43) Date of publication of application:
16.08.90 Bulletin 90/33

(45) Publication of the grant of the patent:
12.05.93 Bulletin 93/19

(64) Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

(56) References cited:
EP-A- 0 026 674
GB-A- 2 048 299
US-A- 2 906 695

(73) Proprietor: **STONE & WEBSTER ENGINEERING CORPORATION**
245 Summer Street P.O. Box 2325
Boston Massachusetts 02107(US)

(72) Inventor: **Gartside, Robert J.**
47 Weston Road
Wellesley Massachusetts 02181(US)

(74) Representative: **Roggero, Sergio et al**
Ing. Barzanò & Zanardo Milano S.p.A. Via
Borgonuovo 10
I- 20121 Milano (IT)

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Description

This invention relates to the production of olefins from hydrocarbon feedstocks. More particularly, the invention relates to the production of olefins by catalytically cracking alone or cracking and dehydrogenating a hydrocarbon. Most particularly the invention relates to a process for cracking hydrocarbons in the presence of an entrained stream of catalytic heat carrying solids at short residence times to preferentially produce olefins having three or more carbon atoms.

It has long been known that naturally occurring hydrocarbons can be cracked at high temperatures to produce valuable olefinic materials, such as ethylene and propylene.

The growth in the propylene based plastics market relative to the ethylene based plastics market has made it desirable to improve the propylene yield when cracking hydrocarbons to olefins.

In addition, higher order olefins, e.g., C_4 olefins, are important precursors for providing high octane blending components, i.e., C_4 's are precursors to MTBE production and alkylation.

However, when heavy hydrocarbons feedstocks are non-catalytically cracked to olefins it's virtually impossible to achieve the desired co-product ratios to fit market needs, i.e. propylene to ethylene yield ratios are rarely greater than 0.55. Higher ratios are attainable only at low hydrocarbon conversion which represents a significant processing penalty in terms of recycle costs and feed degradation. One well-known non-catalytic cracking process is pyrolysis which typically takes place in the presence of steam at high temperatures. The mechanism by which pyrolysis to olefins is achieved is explained in terms of a free radical mechanism.

At high temperatures, radical initiation takes place by homolysis of a carbon-carbon bond. Once initiated the free radicals undergo two principal reactions. They are (1) scission at the beta position of the radical and (2) abstraction of a hydrogen, resulting in termination of the reaction.

The scission at the beta position will continue to the point where a methyl radical will be formed at 90 percent frequency. The methyl radical will then abstract a hydrogen atom from another molecule to form methane and another free radical. Ethylene and methane are the principal products from such free radical pyrolysis reactions. Only about 10 percent of the time will a longer radical abstract a hydrogen from a molecule to form C_3 to C_7 paraffins and olefins. Thus, thermal cracking results in high yields of ethylene relative to higher order olefins with the higher order olefins occurring principally as a result of hydrocarbon branching in the initial hydrocarbon feedstock.

One effort at producing increased production of C_3 and higher olefins is directed to subjecting a light hydrocarbon comprising at least one alkane to cracking conditions in the presence of hydrogen sulfide and a solid contact material comprising silica (US-A-4 471 151 (Kolts)). The contact material employed, such as silica gel, preferably has a high surface area i.e. at least 50 m²/g. Typical H_2S concentrations of 0.1 to 10 mole percent based on the alkane feed are employed in the process. It is theorized in Kolts that the improvement in cracking is due to the high surface area material which acts as a catalyst to decompose H_2S . The result is increased conversion levels with improved selectivity to desired products. However, the improved selectivity to propylene was demonstrated only when cracking n-butane.

The solid contact material employed in Kolts is suitable only for fixed bed operations and not for fluidized bed environments due to its very low mechanical stability. Thus, the solid catalyst of Kolts continues to have the drawbacks of typical catalytic dehydrogenation catalysts designed for fixed beds. These are larger size, diffusion limited catalysts incapable of continuous regeneration in a circulating loop system.

A fluidized catalytic cracking (FCC) unit may also be employed to catalytically produce C_3 and higher compounds. The FCC unit uses acidic cracking catalysts to increase the production of C_3 to C_7 compounds through a carbonium ion mechanism compared to the free radical pyrolysis reaction mechanism. However, the acidic cracking activity of the catalysts, in addition to promoting cracking and isomerization, promotes rapid hydrogen transfer resulting in high yields of paraffins rather than olefins. Further, the nature of the catalytic cracking unit itself favors the shift to paraffins.

The typical definition of residence time in a catalytic cracking operation is the time the feedstock is in contact with the catalyst itself. This definition is acceptable if the temperatures are low such that thermal reactions do not occur to any appreciable extent. However, thermal and catalytic reactions proceed in parallel. While catalyst separation will terminate the catalytic portion of the reaction, the thermal reactions (pyrolysis) will continue until the temperature is reduced to a level where the rate of reaction is insignificant (quench). In this situation, the total kinetic residence time can be defined as the time from the introduction of the hydrocarbon into the system to the quenching of the effluent including the separation of the solids from the reaction. Total conversion is thus the summation of the catalytic reaction (time in contact with the catalyst) and the thermal reactions (time at the reaction temperature).

The typical FCC reaction environment has relatively long residence times including time for solids separation (normally greater than one second) and does not include a quench. Cracking takes place at lower temperatures under these longer residence times. Conversion is achieved at these lower temperatures due to the extended contact with the catalyst. Thermal reactions are minimized at these lower temperatures thus eliminating the need for quenching the effluent. While increased C_3 and higher compounds are produced in comparison to pyrolysis, the effluent will have a disproportionately high concentration of paraffins due to the increased hydrogen transfer activity. The favored conditions for olefin production, specifically higher temperatures and shorter residence times, are difficult to achieve especially when processing light feedstocks such as LPG and naphthas which require proportionately higher temperatures to initiate and sustain the reaction (either catalytic or thermal).

The above processes all improve the cracking of hydrocarbons to olefins. However, these processes suffer either from high capital and operating costs associated with fixed bed operations and hydrogen sulfide dilution, or result in low yields of the desired olefins. In addition, the use of hydrogen sulfide as a diluent raises environmental and health concerns because of its extremely high toxicity.

US-A-2 906 695 discloses a high-temperature, short-time hydrocarbon conversion process in which the hydrocarbon feed is contacted with fluidized particulate solids at a temperature of from 538°C to 649°C in the initial section of a reactor, the resultant reaction mixture is caused to flow rapidly through the reaction zone and receives a strong rotational motion about the axis of the flow, additional highly heated particulate solids being introduced immediately thereafter in the central portion of the fluid mixture so as to heat the mixture to a temperature of from 677°C to 982°C.

GB-A-2 048 299 discloses a catalytic cracking process in which hydrocarbons having a boiling point above 220°C are converted into lower boiling hydrocarbon products of improved octane rating with the aid of a particulate crystalline catalyst having pore opening and maximum cage dimensions of 55 nm to 70 nm, an active dehydrogenating metal being disposed within the interior of the crystals. EP-A-0 26 674 discloses an improved sequential Thermal Regenerative Cracking (TRC) process, together with an improved solids quench procedure, an improved preheat vaporization system and an improved fuel gas generation system.

It has now been found that the higher order olefins, i.e. propylene, butenes, etc. can be obtained in high yields by the cracking of hydrocarbons in the presence of an acidic cracking catalyst in combination with a noble metal oxide dehydrogenation catalyst in a short residence time fluidized solids cracking environment. This short residence time is achieved by a combination of a low residence time reactor, a very short residence time separation system, and a product quench.

It is therefore an object of the present invention to provide a process in which hydrocarbons can be catalytically cracked to produce olefins.

It is another object of the present invention to provide a process for preferentially cracking hydrocarbons to obtain C_3 to C_5 olefins.

It is a further object of the present invention to provide a reaction system including a quenching step for preferentially cracking hydrocarbons to obtain C_3 to C_5 olefins while avoiding the thermal degradation of products.

The present invention relates generally to a process for preferentially cracking hydrocarbons to obtain olefins, preferably C_3 to C_5 olefins, at the acid sites of catalyst solids and catalytically dehydrogenating the resulting paraffin isomers to thereby produce olefins. This invention now provides a process for catalytically cracking a hydrocarbon feedstock to selectively produce C_3 to C_5 olefins, comprising the steps of:

- (a) introducing the hydrocarbon feedstock to a cracking reactor;
 - (b) simultaneously delivering hot very high activity acid cracking catalyst solids to the cracking reactor;
 - (c) catalytically and thermally cracking the hydrocarbon feedstock with heat supplied by the hot very high activity acidic catalyst solids to form a cracked product;
 - (d) separating the cracked product from the hot catalyst solids, and
 - (e) quenching the separated cracked product,
- characterized in that the total kinetic residence time of the hydrocarbon feedstock from step (a) to step (e) is of from 0.05 s to 2.0 s, the temperature of the cracking reaction is of from 482°C to 815°C, the pressure of the cracking reactor is of from 0.69 bar to 6.9 bar (10 psi to 100 psi), the weight ratio of the catalyst solids to the hydrocarbon feedstock is of from 1:1 to 60:1, and the very high activity acidic cracking catalyst is a zeolitic catalyst associated with a dehydrogenation catalyst consisting of a metal oxide selected from the oxides of iron, chromium, tin, or platinum on an inert carrier.

Acidic catalytic cracking of hydrocarbons proceeds by a carbonium ion mechanism unlike the free radical mechanism of thermal cracking. The carbonium ion is formed by the abstraction of a hydride ion from the carbon-hydrogen bond. The abstraction of the hydride ion and the creation of a carbonium ion

is catalyzed by the acid sites on the catalyst solids.

Carbonium ion cracking also occurs at the beta position thereby leading to the formation of an olefin and a primary carbonium ion. The primary carbonium ion undergoes a rapid ionic shift (isomerization) to produce a secondary or tertiary carbonium ion. This coupled with the beta cracking rule leads to the formation of propylene in high yields without the concurrent production of significant amounts of ethylene. Any ethylene found in the product is the result of the competitive free radical cracking route. In addition to providing the carbonium ion mechanism for isomerization, the acidic sites on the catalyst promote hydrogen transfer. Thus, while the thermodynamic equilibrium conditions at the temperatures contemplated in the invention favor olefins over paraffins, the increased hydrogen transfer activity may result in a disproportionately high paraffin yield. This is especially true for the branched isomers such as isobutylene. In these cases, if a specific dehydrogenation catalyst is used in combination with an acidic cracking catalyst, the yield distribution can be shifted toward the thermodynamic equilibrium and higher concentrations of the desired olefins can be obtained.

For the purpose of this invention, the kinetic residence time is defined as the total time from the point where the hydrocarbon is introduced to the reactor zone to the point where the cracked products are quenched, including the intermediate separation step. This distinguishes the present process from other processes where measurement of the residence time is terminated prior to the point of separation and quench. This is especially important since the catalytic cracking of hydrocarbons always proceeds in parallel with pyrolysis. The extent to which products are formed catalytically or thermally is a function of catalyst activity, catalyst loading, catalyst residence time, reaction temperature profile, and the total kinetic residence time in the thermal-catalytic environment. For example, mild acidic catalytic activity at higher temperatures could be used to shift diolefin production to paraffins and olefins without substantially altering the ratio of the carbon products obtained by pyrolysis. Alternatively, very highly active acidic cracking catalysts could be used at significantly lower temperatures to minimize the thermal route and maximize the acidic catalyst product distribution. Further, it has been found that catalytic dehydrogenation catalysts can be used in combination with the acidic cracking catalysts to shift the reaction in favor of olefin production.

The present invention is particularly well suited for cracking hydrocarbon feedstocks such as C₄ - C₇ paraffins, naphthas, and light gas oils to higher order olefins, i.e., having three to five carbon atoms. However, it should be noted that the process has general applications for cracking the entire range of hydrocarbons from light distillates to heavy resids.

The process of the present invention proceeds by delivering a preheated hydrocarbon feedstock and steam to the top of a downflow tubular reactor. Simultaneously, hot catalyst solids are introduced to the top of the reactor and the combined stream of hydrocarbon, steam and catalyst solids pass through the reactor zone, a separation zone, and a quench zone where the hydrocarbon undergoes cracking at low severity and short residence times and the effluent is stabilized to prevent product degradation.

The tubular reactor is operated at a temperature of 482°C to 816°C (900°F to 1500°F), preferably 538°C to 704°C (1000°F to 1300°F) and at a pressure of 0.69 bar to 6.9 bar (10 to 100 psia) with a total kinetic residence time of about 0.05 to 2.0 s, preferably about 0.10 to 0.5 s.

After separation from the cracked effluent the catalyst solids are stripped of residual hydrocarbon, regenerated and reheated in a transfer line and returned to the tubular reactor to continue the cracking process.

The present invention is particularly well adapted for use in a short residence time fluidized solids cracking apparatus and in a short residence time separation apparatus, as described in US - A - 4 370 303 (Woebcke et al), US - A - 4 433 984 (Gartside et al).

The specific catalyst solids and the catalyst to hydrocarbon ratio are chosen based on the feedstock characteristics and the product distribution desired. Catalyst activity and catalyst loading will define operating temperatures at the short residence times employed in the present invention and thus determine the split between the catalytic and thermal reactions. The catalyst type, either acidic cracking alone or in combination with noble metal oxide dehydrogenation, will further determine the product distribution between olefins and paraffins.

The process of the present invention will be better understood when considered with the following drawings, wherein:

FIGURE 1 is a schematic view of the process scheme of the present invention;

FIGURE 2 is a cross-sectional elevational view of the reactor feeder employed in the apparatus of the present invention;

FIGURE 3 is a cross-sectional elevational view of the separator employed in the present invention;

FIGURE 4 is a sectional view through line 4-4 of FIGURE 3.

FIGURE 5 is a schematic view of an optional quenching process scheme of the present invention;

FIGURE 6 is an elevational view of one embodiment of the overall system of the present invention;
 FIGURE 7 is a cross-sectional elevational view of one embodiment of the reactor and gas-solids separator employed in the present invention;
 FIGURE 8 is a sectional plan view through line 8-8 of FIGURE 7; and
 FIGURE 9 is a schematic elevational view of another embodiment of the solids regeneration assembly employed in the present invention.

As has been previously indicated, the process of the present invention is directed to a means for cracking hydrocarbon feedstocks in the presence of catalytically active heat carrying solids for the purpose of producing olefins with a high selectivity towards C_3 to C_5 olefins.

The hydrocarbons contemplated as feedstocks include the high boiling distillate gas oils, atmospheric gas oils, naphthas, and C_4 - C_7 paraffins. However, it should be noted that the process has general applications for catalytically cracking a wide range of hydrocarbons to produce the desired olefins.

Referring to the drawings and first to FIGURE 1, the process of the present invention can be performed in a short residence time fluidized solids cracking system 1, hereinafter QC system, incorporating a tubular reactor 2, a reactor feeder 4, a separator 6, a quench means 24 and a solids stripper 8.

The system 1 also includes means for regenerating the catalyst solids separated from the cracked product after the reaction. The system shown illustratively includes an entrained bed heater 10 wherein the catalyst solids can be regenerated and reheated, a transport line 12 and a fluid bed vessel 14 wherein the solids are stripped of combustion gases and again distributed to the reactor 2.

In operation, hot catalyst solids from the fluid bed vessel 14 enter the reactor feeder 4 and are admixed with steam entering through a line 16. The hydrocarbon feed is delivered through a line 18 to a preheater 20, then through a line 22 to the upper region of the tubular reactor 2. The preheated hydrocarbon feed along with the catalyst solids and steam from the reactor feeder 4 are passed through the tubular reactor 2. Intimate mixing of the hot catalyst solids, steam and preheated hydrocarbon occurs in the reactor and cracking proceeds immediately.

Upon exiting the tubular reactor 2 the cracked hydrocarbon effluent and steam are immediately separated from the catalyst solids in the separator 6 and the cracked effluent product passes overhead through the quench area 24 where the cracked product is immediately quenched with steam or a light hydrocarbon delivered to the quench area 24 through a quench line 26. This reduces the temperature of the mixture below the point where substantial thermal reactions occur. Alternatively, the cracked product exiting the tubular reactor 2 and separated from the catalyst solids in the separator 6 may be quenched by passing the entire mixture over a bed of solids with catalytic (dehydrogenation) activity. Since dehydrogenation is an endothermic reaction, the flowing mixture will be cooled as the reaction proceeds. This can be used with the introduction of steam to improve the reaction conditions. As seen in FIGURE 5, the preferred method of quenching in this manner includes the use of a catalyst reactor 25, in which the bed of the catalytic solids are contained, located immediately downstream of the separator 6, where quenching occurs in the previous embodiment.

The quenched product is passed through a cyclone 28 where small amounts of entrained catalyst solids are removed and delivered through a line 30 to the solids stripper 8 where they are combined with the bulk of the stripped solids delivered from the separator 6 through a line 32. In the solids stripper 8, the catalyst solids are stripped of residual hydrocarbon by steam, nitrogen or other inert gases delivered to the solids stripper 8 through a line 34.

The catalyst solids, which have accumulated carbon or coke deposits from the tubular reactor 2 are then passed to the entrained bed heater 10. Air delivered to the heater 10 through a line 36 is mixed with the stripped catalyst solids in the heater 10 and the mixture is fed into the transport line 12 for conveying the catalyst solids back to the fluid bed vessel 14. In the presence of air from the line 36, the carbon deposits on the catalyst solids are removed by combustion to provide the heat necessary for the cracking reaction. If additional fuel is required it may be added into the entrained heater 10 from a fuel source (not shown).

In essence, the process of the present invention is conducted by delivering a hydrocarbon such as naphtha, atmospheric gas oil or mixtures thereof, through the line 13 to the preheater 20 wherein the temperature of the hydrocarbon is elevated to 427°C to 482°C (800 - 900°F). Simultaneously, catalyst solids from the fluid bed vessel 14 are delivered to the reactor feeder 4 (best seen in FIGURE 2) where they are admixed with steam supplied through the line 16 and delivered to the reactor at a temperature in the range of 1000 - 1600°F . The catalyst solids to the hydrocarbon feed ratio ranges from 1 to 60:1 based on weight depending on the particular catalyst utilized. The water vapor/hydrocarbon feed ratio is in the range of 0 to 1.0, preferably 0.0 to 0.3.

Optionally, the catalytic cracking process may be initiated by injecting an alkane such as ethane into the tubular reactor 2, via injection line 16, to form olefins and free radicals. This will tend to increase isomerization by forming carbonium ions and stabilize the heavier hydrocarbon formation by competing with the free radicals formed as well. Such alkanes are added just upstream of the hydrocarbon feed 22.

5 A suitable catalyst solids for the present invention may be one of the generally available supports having acid properties such as, silica gel, alumina, clays, etc. The catalyst system employed is a conventional zeolitic FCC catalyst or one of the high activity ZSM-5 or rare earth zeolitic catalysts, including a dehydrogenation catalyst consisting of one of the noble metal oxides such as the oxides of iron, chromium, platinum, etc. on a suitable support such as silica alumina. Alternately, the catalyst could be a
10 mixture of the aforementioned catalysts to achieve specific yield distributions.

The composite hydrocarbon feedstock is elevated to 427°C to 593°C (800 to 1100°F), and the catalyst solids are heated to 649°C to 927°C (1200 to 1700°F) in the tubular reactor 2. The ratio of solids to hydrocarbon is set by heat balance and desired solids catalytic activity.

The cracked effluent product and catalyst solid effluent from the tubular reactor 2 flow directly into
15 separator 6 (best seen in FIGURE 3) where a separation into a gas product phase and a catalyst solid phase is effected. The gas product is removed via the line 24, while the catalyst solids enter the solids stripper 8 through the line 32. An in-line quench of the gas product is provided in quench area 24 through the quench line 26. Cold solids, water, steam, light hydrocarbons, and recycle oils are examples of suitable quench materials. Alternatively, quenching takes place in the catalyst reactor 25 (see FIGURE 5) by passing
20 the product over a catalyst bed, the additional reaction being without the presence of solids.

The total residence time from the point of hydrocarbon introduction to the tubular reactor 2 to the point of quench in the quench area 24, optionally comprising a catalyst reactor 25, is preferably about 0.1 to 0.3 seconds.

In the solids stripper 8 the catalyst solids are stripped of gas impurities by a stream of steam, nitrogen
25 or inert gas delivered through the line 34. Vapors are removed from the solids stripper 8 through the line 30.

The stripped catalyst solids are removed from the stripper 8 through a line 38. The catalyst solids which have accumulated carbon from the tubular reactor 2 are passed to the entrained bed heater 10 where air is delivered through a line 36 to provide the necessary atmosphere for regenerating the catalyst solids. The catalyst solids are entrained in the heater 10 and returned to the fluid bed vessel 14 through the transport
30 line 12 where the catalyst solids continue to regenerate. In addition, the regeneration of the catalyst solids raises the temperature of the catalyst solids to 649°C to 927°C (1200 to 1700°F) prior to delivery of the catalyst to the fluid bed vessel 14.

Details of the reactor feeder 4 are more fully described in US-A-4 338 187 (Gartside et al). The reactor feeder of Gartside et al. has the capability of rapidly admixing hydrocarbon feed and catalyst solids.
35 As seen in FIGURE 2, the reactor feeder 4 delivers catalyst solids from a solids receptacle or fluid bed vessel 70 through vertically disposed conduits 72 to the tubular reactor 2 and simultaneously delivers hydrocarbon feed to the tubular reactor 2 at an angle into the path of the catalyst solids being discharged from the conduits 72. An annular chamber 74 to which hydrocarbon is fed by a single entry comprising a toroidal feed line 76 terminates in angled openings 78. A mixing baffle or plug 80 also assists in effecting
40 rapid and intimate mixing of the hydrocarbon feed and the catalyst solids. The edges 79 of the angled openings 78 are preferably convergently beveled, as are the edges 79 at the reactor end of the conduits 72. In this way, the gaseous hydrocarbon stream from the chamber 74 is angularly injected into the mixing zone and intercepts the catalyst solids phase flowing from the conduits 72. A projection of the gas would form a cone shown by dotted lines 77, the vortex of which is beneath the flow path of the solids. By introducing the
45 gaseous hydrocarbon phase angularly, the two phases are mixed rapidly and uniformly, and form a homogeneous reaction phase.

The mixing of a solid phase with a gaseous phase is a function of the shear surface between the solids and gas phases, and the flow area. A ratio of shear surface to flow area (S/A) of infinity defines perfect mixing while poorest mixing occurs when the solids are introduced at the wall of the reaction zone. In the
50 system of the present invention, the gas stream is introduced annularly to the solids which ensures high shear surface. By also adding the gas phase transversely through an annular feed means, as in the preferred embodiment, penetration of the phases is obtained and even faster mixing results. By using a plurality of annular gas feed points and a plurality of solid feed conduits, even greater mixing is more rapidly promoted, since the shear surface to flow area ratio for a constant solids flow area is increased.
55 Mixing is also a known function of the length to diameter ratio of the mixing zone. A plug creates an effectively reduced diameter D in a constant length L, thus increasing mixing.

The plug 80 reduces the flow area and forms discrete mixing zones. The combination of annular gas addition around each solids feed point and a confined discrete mixing zone greatly enhances the conditions

for mixing. Using this preferred embodiment, the time required to obtain an essentially homogenous reaction phase in the reaction zone is quite short. Thus, this preferred method of gas and solids addition can be used in reaction systems having a residence time below 1 second, and even below 100 milliseconds. Because of the environment of the tubular reactor 2 and the reactor feeder 4, the walls are lined with an inner core 81 of ceramic material.

The separator 6 of the QC system, as shown in FIGURE 3, can also be relied on for rapid and discrete separation of product and catalyst solids discharging from the tubular reactor 2. The inlet to the separator 6 is directly above a right angle corner 90 at which a mass of catalyst solids 92 collect within a chamber 93. An optional weir 94 downstream from the right angle corner 90 facilitates accumulation of the mass of solids 92 especially when run on small scale rather than commercial scale production. The gas outlet 24 of the separator 6 is oriented 180° from a separator gas - solids inlet 96 and the solids outlet line 32 is directly opposed in orientation to the gas outlet 24 and downstream of both the gas outlet line 24 and the weir 94.

In operation, centrifugal force propels the catalyst solids to the wall opposite inlet 96 of the chamber 93 while the gas portion having less momentum, flows through the vapor space of the chamber 93. Initially, catalyst solids impinge on the wall opposite the inlet 96 but subsequently accumulate to form a static bed of solids 92 which ultimately form in a surface configuration having a curvilinear arc of approximately 90° of a circle. Solids impinging upon the bed 92 are moved along the curvilinear arc to the solids outlet 95, which is preferably oriented for downflow of solids by gravity. The exact shape of the arc is determined by the geometry of the particular separator and the inlet stream parameters such as velocity, mass flowrate, bulk density, and particle size. Because the force imparted to the incoming solids is directed against the static bed 92 rather than the separator 6 itself, erosion is minimal. Separator efficiency, defined as the removal of solids from the gas phase leaving through the outlet 97, is therefore, not affected adversely by high inlet velocities, up to 45.75 m/s (150 ft./sec.), and the separator 6 is operable over a wide range of dilute phase densities, preferably between 0.016 to 0.16 g/cm³ (0.1 and 10.0 lbs./ft.³). The separator 6 of the present invention achieves efficiencies of about 90%, although the preferred embodiment, can obtain over 97% removal of catalyst solids.

It has been found that for a given height H of the chamber 93, efficiency increases as the 180° U-bend distance between the inlet 96 and the outlet 97 is brought progressively closer to the inlet 96. Thus, for a given height H the efficiency of the separator 6 increases as the flow path decreases and, hence, residence time decreases. Assuming an inside diameter D_i of the outlet 96, the distance CL between the centerlines of the inlet 96 and the outlet 97 is preferably not greater than 4.0(D_i), while the most preferred distance between said centerlines is between 1.5 and 2.5(D_i). Below 1.5(D_i) better separation is obtained but difficulty in fabrication makes this embodiment less attractive in most instances. Should this latter embodiment be desired, the separator 6 may require a unitary casting design because the inlet 96 and the outlet 97 would be too close to one another to allow welded fabrication.

It has been found that the height H should be at least equal to the value of 1.5 x D_i or 10.16 cm (4 inches) in height, whichever is greater. Practice teaches that if H is less than D_i or 10.16 cm (4 inches) the incoming stream is apt to disturb the bed solids 92 thereby reentraining solids in the gas product leaving through the outlet 97. Preferably the height H is on the order of twice D_i to obtain even greater separation efficiency. While not otherwise limited, it is apparent that too large a height H eventually merely increases residence time without substantive increases in efficiency. The width W shown in FIGURE 4 of the flow path is preferably between 0.75 and 1.25 times D_i, most preferably between 0.9 and 1.10 (D_i).

The outlet 97 may be of any inside diameter (Dog). However, velocities greater than 23 m/s (75 ft./sec.) can cause erosion because of residual solids entrained in the gas. The inside diameter Dog of the outlet 97 should be sized so that a pressure differential between the solids stripper 8 shown in FIGURE 1 and the separator 6 exists such that a static height of solids is formed in the solids outlet line 32. The static height of solids in the solids outlet line 32 forms a positive seal which prevents gases from entering the solids stripper 8. The magnitude of the pressure differential between the solids stripper 8 and the separator 6 is determined by the force required to move the solids in bulk flow to the solids outlet 95 as well as the height of solids in the line 32. As the differential increases the net flow of gas to the solids stripper 8 decreases. Solids, having gravitational momentum, overcome the differential, while gas preferentially leaves through the gas outlet 97. Preferably, the inside diameter Dog of the gas outlet 97 is the same as the inside diameter of the inlet 96, when one outlet is employed, to provide outlet velocity less than or equal to inlet velocity.

FIGURE 4 shows a cutaway view of the separator 6 along section 4-4 of FIGURE 3. It is essential that longitudinal side walls 101 and 102 be rectilinear, or slightly arcuate as indicated by the dotted lines 101a and 102a. Thus, the flow path through the separator 6 is essentially rectangular in cross-section having a height H and width W as shown in FIGURE 4. The embodiment shown in FIGURE 4 defines the geometry

of the flow path by adjustment of the lining width for the walls 101 and 102. Alternatively, baffles, inserts, weirs or other means may be used. In like fashion the configuration of the walls 103 and 104 transverse to the flow path may be similarly shared, although this is not essential.

The separator shell and manways are preferably lined with erosion resistant linings 105, which may be required if solids at high velocities are encountered. Typical commercially available materials for erosion resistant linings include Carborundum Precast Carbofrax D' (Reg. Trade Mark), Carborundum Precast Alfrax 201 (Reg. Trade Mark) or their equivalent. A thermal insulation lining 106 may be placed between the shell and the lining 105 and between the manways and their respective erosion resistant linings when the separator 6 is to be used in high temperatures service.

The details of the separator 6 are more fully described in US - A - 4 288 235.

Referring to the drawings and particularly to FIGURES 6-9, there is described a system 202 comprising a reactor system 204, a solids regeneration assembly 208 and a solids delivery system 210.

The reactor system 204, best seen in FIGURE 7, includes a convergent mixing section 211, an elongated reaction section 212, a divergent section 213 downstream of the elongated reaction section 212, a separator 206 and a quench system 207 (shown in FIGURE 8). The mixing sections 211 are formed with a plug section 214 shown in cross-section as having an arcuate lower surface 215. A horizontally disposed plate 217 is arranged over the plug section 214 in spaced-relationship with the plug section 214 to form solids inlet passages 219 to the interior of the mixing section 211. The solids inlet passages 219 are configured in cross-section with a right angle turn and terminate in a rectangular openings 225 through which the particulate solids enter the mixing section 211, in the form a curtain of solids 226. The horizontal openings 225 are directly above each hydrocarbon feed inlet. Venturi configured passages 203 extend from the solids inlet passages 219 to the hydrocarbon feed inlets 228.

Steam plenums (not shown) are arranged along each longitudinal edge of the horizontal opening 225 to deliver pre-acceleration gas (steam) through nozzles (not shown) into the curtain of solids 226 passing through the horizontal openings 225. A gas delivery line (not shown) is provided to deliver gas, usually steam or light hydrocarbon, under pressure to the nozzles. The nozzles are arranged at a downward angle of 45° to the horizontal. The pre-acceleration gas is delivered to the plenums at pressures of 3 to 5 psi above the pressure in the reactor and discharges through the nozzles at the same relative pressure at a velocity of about 150 feet per second. The pre-acceleration gas accelerates the flow of solids through the horizontal openings 225 from a nominal three to six feet per second to approximately 50 feet per second for the mix of solids and pre-acceleration gas.

The hydrocarbon feed inlets 228 are located on the reactor wall arranged either normal to the solids curtain 226 or at an angle upwardly of 30° into the solids curtain 226. The hydrocarbon feed is delivered to a manifold 223 through a line 224. The feed inlet nozzles 228 are fed with hydrocarbon from the manifold 223. As seen in FIGURE 7, the feed inlet nozzles 228 are diametrically opposed from each other in the same horizontal plane. The mixing zone 211 of the reactor is rectangular with the configuration making a transition to a tubular reactor at the elongated reaction section 212.

The feedstock entering the mixing zone 211 through nozzles 228 immediately impinge the solids curtains 226 and the desired mixing of feed and hot particulate solids occurs. With the opposing set of nozzles 228, the opposing feed jets and entrained solids from the solids curtain 226 will be directed by the arcuate contour 215 of the plug section 214 and impact with each other at approximately the vertical centerline of the mixing zone 211. When a gas-liquid mixed phase hydrocarbon is fed through the nozzles 228, the nozzles 228 are arranged at an angle normal or 90° to the solids curtain 226. When the hydrocarbon feed is a gas, the nozzles 228 are arranged at an upwardly directed angle of 30° into the solids curtain. The quantity of solids entering the mixing zone 211 of the reactor system 204 through the horizontal inlets 219 is controlled in large part by the pressure differential between the mixing zone 211 of the reactor system 204 and the chamber 231a above the solids reservoir 218 in a solids control hopper 231 directly above the horizontal inlets 219. Pressure probes 233 and 235 are located respectively in the mixing zone 211 of the reactor system 204 and the control hopper chamber 231a to measure the pressure differential. Gas (steam) under pressure is delivered through a line 230 to the control hopper chamber 231a to regulate the pressure differential between the mixing zone 211 of the reactor system 204 and the control hopper chamber 231a to promote or interrupt flow of the solids from the solids control hopper 231 to the mixing zone 211.

As best seen in FIGURE 7, the separator 206 is comprised of a mixed phase inlet 232, a horizontal chamber section 234, a plurality of cracked gas outlets 236 and particulate solids outlets 238. The basic principles relating to relative diameters (Di, Dog, Dos), chamber height (H) and length (L) recited in the first embodiment described herein are applicable herein. The separator 206 is arranged in combination with the elongated cracking zone 212 and divergent section 213 of the reactor system 204. The divergent section

213 terminates in the separator mixed phase inlet 232 which is centrally disposed at the top of the horizontal section 234. As a result of the configuration of the composite reaction system including the separator 206, a solids bed 242 develops on the floor 240 of the horizontal section 234 with the cross-sectional profile 243 of the bed 242 forming a curvilinear arc over which the mixed phase gas and solids travel. The expansion of solids and cracked gas in the divergent section 213 enhances heat transfer and limits the velocity of the solids - gas mixture entering the separator 206.

The solids are sent to the lateral ends 246 of the horizontal section 234 and discharge downwardly through the solids outlets 238. The cracked gases follow a 180° path and after separation from the solids discharge through gas outlets 236 that are located on the top of the horizontal section 234 intermediate the lateral ends 246. The plurality of solids outlets 238 and gas outlets 236 provide simultaneously for both minimum time in the separation zone and maximum solids - gas separation.

The separation or quench system 207 also includes a conventional cyclone separator 250 directly downstream of each gas outlet 236, as best seen in FIGURE 8. The entry line 254 to each cyclone separator 250 is arranged at an angle of 90° to the gas outlet 236 with the cyclone separator 250 vertically disposed in the system. The cyclone separators 250 serve to collect the remaining entrained particulate solids from the cracked gas discharged from the separator 206. A dipleg line 249, returns the particulate solids to the regeneration assembly 208 and the cracked gas is sent for downstream processing through the gas outlet 251.

Each cyclone entry line 254 extending from the cracked gas outlet 236 to the cyclone 250 is provided with a direct quench line 252. Quench oil, usually the 38°C - 204°C (100 - 400°F) cut from a downstream distillation tower is introduced into the cyclone 250 through the direct quench line 252 to terminate the reactions of the cracked gas.

As best seen in FIGURE 9, the regeneration assembly 208 is comprised of a stripper 253, control hopper 255, entrained bed heater 258, a lift line 257, and a regenerated solids vessel 260.

The stripper 253 is a tubular vessel into which the particulate solids from the separator 206 are delivered through solids outlet legs extending from the separator solids outlets 238 and from the cyclone diplegs 249. A ring 262 having nozzle openings 264 is provided at the bottom of the stripper 253. A stripping gas, typically steam is delivered to the ring 262 for discharge through the nozzles 264. The stripping steam passes upwardly through the bed of particulate solids to remove impurities from the surface of the particulate solids. The stripping steam and entrained impurities pass upwardly through the particulate solids in the stripper 253 and discharge through a vent line (not shown) to the cracked gas line.

The stripped solids are accumulated in the control hopper 255 for eventual delivery to the entrained bed heater 258. The control hopper 255 is a collection vessel in which solids enter through a standpipe 266 and from which an outlet line 273 extends to deliver solids to the entrained bed heater 258. The assembly of the control hopper 255 and the standpipe 266 provides for a slumped bed solids transport system. The pressure differential maintained between the slumped bed surface 268 in the control hopper 255 and the exit 270 of the outlet line 273 determine the solids flow rate between the control hopper 255 and the entrained bed heater 258. A line 272 is provided to selectively introduce steam under pressure into the control hopper 255 to regulate the pressure differential. Probes 267 and 269 are placed respectively in the control hopper 255 and entrained bed heater 258 to monitor the pressure differential and regulate a valve 265 in the steam line 272.

The entrained bed heater 258 is essentially tubular in configuration. An array of distinct fuel nozzles 261 fed by fuel lines 263 are arranged essentially symmetrically on the lower inclined surface 275 of the entrained bed heater 258. Pressurized air enters the entrained bed heater 258 through a nozzle 277 arranged to direct the air axially upwardly through the entrained bed heater 258. The air jet provides both the motive force to lift the solids particles upwardly through the entrained bed heater 258 to the regenerated solids vessel 260 and the air necessary for combustion. The fuel is ignited by contact with the solids in the presence of air.

The combustion gas/solids mixture moving upwardly through lift line 257 enters the regenerated solids vessel 260 tangentially, preferably, perpendicular to the lift line to separate the combustion gases from the solids. As shown in FIGURE 6, the vessel 260 has a distube 285 in the gas outlet nozzle 286 to provide cyclonic movement which improves the separation efficiency of the system.

The regenerated solids vessel 260 is a cylindrical vessel provided with a standpipe 271, seen in FIGURE 7, extending to the reactor hopper 231. Again the structure of the regenerated solids vessel 260 provides for accumulation of a slumped bed 281, seen in FIGURE 9 above which pressure can be regulated to enable controlled delivery of the regenerated particulate solids to the reactor hopper 231.

The upper solids collection vessel 260 seen in FIGURES 6, 7 and 9 contains a stripping section as the lower portion with a stripping ring 279 and form a part of the solids deliver system 210. Above ring 279, the

solids are fluidized; below the ring 279 the solids slump and are fed to the standpipe 271 shown in FIGURE 7. The standpipe 271 feeds the slumped bed in the control hopper 231 as best seen in FIGURE 7. Solids flow into the reactor hopper 231 through the standpipe 271 to replace solids that have flowed into the reactor 204. Unagitated solids (slumped solids) will not continue to flow into the reactor hopper 231 once the entrance 282 to the hopper 231 has been covered. Thus, the position of the entrance 282 defines the solids level in hopper 231. As solids flow from hopper 231 via the pressure differential between the vapor space in the chamber 231a above the bed 218 and the mixing zone 211, the entrance 282 is uncovered allowing additional solids to flow into the hopper 231.

One embodiment of the process of the present invention as shown in the accompanying FIGURE 1 is illustrated by the following comparative example (Table I) wherein a light FCC naphtha is cracked employing conventional tubular pyrolysis, conventional catalytic cracking at typical FCC residence times of greater than 1 second using moderately active catalysts, catalytic cracking with high activity catalysts at short residence times for FCC units (0.9 seconds), and very short residence time cracking plus quench (QC system) with a similar high activity catalyst. Two cases employing the high activity catalyst are shown to illustrate the effect of residence time on olefin yields.

TABLE I

	Light FCC Naphtha			
	Conventional Coll Pyrolysis	Cat Cracker Con- tional Catalyst	Catalytic Cracker High Activity Catalyst	QC with High Activity Catalyst
	A	B	C	D
Example:				
Feedstock:				
Residence Time, s				
Reactor	0.3 s	1.0 s		
Total (to quench)	0.3 s	2.0 s	0.9*	0.15
Reactor Temperature °C	816°C	565°C	510°C	540°C
Conversion, Wt%	65	28	50	56
Product Yield, Wt%				
C ₁₁ H ₄	13.4		3.0	0.8
Total C ₂ 's	15.2	2.6	13.0	11.2
C ₃ H ₆	11.4	5.6	10.2	19.2
C ₃ H ₈	0.6	4.1	11.6	8.8
Total C ₄ 's	10.4	13.4	7.7	14.4
C ₃ H ₈ /C ₃ H ₆ ratio**	0.05	0.73	1.14	0.46

* no quench

** paraffin/olefin ratio

Referring to Table I, Example A illustrates the yields obtainable using conventional pyrolysis operated at typical thermal cracking temperatures and residence times. Example B illustrates a conventional catalytic riser reactor employing typically longer residence times and lower temperatures than the pyrolysis Example A. As seen, the conventional catalytic conversions are substantially lower than those obtained in the pyrolysis Example A. The lower conversion is a result of the lower temperature operation (565°C vs.

816°C) with insufficient catalytic activity for this relatively light feedstock. Even at these low conversions however, the total C₃ and C₄ compounds are high relative to the pyrolysis case as a result of the carbonium ion mechanism. Further, the ratio of C₃ paraffins to C₃ olefins is substantially increased due to hydrogen transfer activity of the acidic cracking catalyst.

5 Example C illustrates the product yields which will be obtained by employing high activity acidic catalysts at low FCC residence times or high QC residence times without quenching. The selected operating conditions of Example C will result in a suppression of the methane and ethylene yields compared to the pyrolysis system of Example A. The conversion is increased relative to Example B even at lower temperatures (510°C vs. 565°C) due to the increased activity. There is a significant increase in the
10 total C₃ production as a result of the acidic cracking catalyst (21.8 vs. 12.0) but the C₄ yields decrease due to the increased conversion. Further, due to the longer residence times, there is a significant amount of hydrogen transfer as evidenced by the unacceptably high C₃ paraffin to olefin ratio compared to either Example A or B.

Example D illustrates the dramatic improvement in olefin yields that will be obtained by employing the
15 process of the present invention in a very short residence time QC system. As seen, there is about a 100% improvement in C₃ olefin yields when the reactor temperature is increased about 30°C and the total kinetic residence time, i.e., cracking reaction plus separation plus quench, is reduced to about 0.15 seconds. In addition, the paraffins to olefin ratio is reduced to less than half that obtained in the longer residence time Example C. The paraffin to olefin ratio for this case is higher than for the pyrolysis case at a similar
20 residence time as a result of the hydrogen transfer activity of the catalyst. The methane yield, however, is further suppressed below the lower level of Example C and the C₄ yields are improved by almost 100% indicating less secondary cracking due to the quenching and short residence time reaction.

In another embodiment of the invention a dehydrogenation catalyst is combined with an acidic cracking catalyst.

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TABLE II
MINAS NAPHTHA CRACKING

	Coil Pyrolysis	Moderate Activity Acidic Cracking Catalyst	Yield with Catalyst Yield from Coil Cracking
Residence Time	0.2 s	0.2 s	
Temp °C	827	746	
Yield, wt%			
CH ₄	12.5	9.5	0.76
C ₂ H ₄	23.0	17.3	0.75
C ₂ H ₆	3.7	2.8	0.76
C ₃ H ₆	13.4	13.7	1.20
C ₃ H ₈	0.5	3.0	1.20
C ₄ H ₆	4.2	0.7	
C ₄ H ₈	4.5	7.3	1.53
C ₄ H ₁₀	0.7	6.7	
	62.5	61.0	

The example shown in Table II uses a Minas naphtha feedstock and compares cracking both catalytically and thermally. The catalytic case requires a lower temperature to achieve the given conversion thus will have in this case only 75% of the thermal products (C₁ and C₂ compounds). The carbonium ion cracking will shift the yield spectrum to favor C₃ and C₄ compounds.

TABLE III

ISO/NORMAL C ₄ YIELDS FROM MINAS NAPHTHA CRACKING (REFERENCE TABLE II)			
	Coil Pyrolysis	Acidic Cat Only	Acidic Cat plus* Dehydrog Cat
I-C ₄ H ₈	1.5	1.84	5.02
N-C ₄ H ₈	3.0	5.44	6.71
I-C ₄ H ₁₀	0.23	4.43	1.25
N-C ₄ H ₁₀	0.47	2.28	1.00
Iso (% olefin)	87	29	80
Nor (% olefin)	87	70	87

* Mixture of Sn and Cr oxides on an alumina support

As shown in Table III, use of acidic catalyst alone results in a very significant increase in total iso C₄'s (paraffins plus olefins) due to the ionic nature of the cracking. However, most of the iso compounds appear as iso-paraffins whereas the thermodynamic equilibrium exclusively favors the production of olefins, not paraffins. In the case of the coil pyrolysis, both the iso and normal C₄'s are 87% olefinic indicating a

reasonable approach to equilibrium. For the catalyst case however, the normal compounds are only 70% olefinic and the iso compounds only 29% olefinic. This is because the hydrogen transfer activity of the catalyst results in a "new" equilibrium relationship based on reaction kinetics rather than thermodynamics. Iso compounds show a much greater tendency to undergo hydrogen transfer in the presence of the acidic catalyst than normal compounds.

When noble metal oxide catalysts are added to the flowing acidic cracking catalysts, the paraffins produced at the acidic sites can be dehydrogenated to their olefinic counterpart. The extent to which this occurs is dependent upon the concentration and activity of the dehydrogenation catalyst. In Table III, a dehydrogenation catalyst consisting of oxides of tin (Sn) and chromium (Cr) is mixed with the acidic cracking catalyst to achieve an 80% approach to equilibrium for the iso compounds and a corresponding 87% approach for the normal compounds. As can be seen, the production of the valuable C₄ olefins, both normal and iso, are significantly increased. The isobutylene production from the same feed is increased by a factor of over 3 and the normal butene by a factor of over 2. The use of mixed catalyst systems provides an additional product distribution flexibility for the catalytic process. Rather than admix the dehydrogenation catalyst with the acidic cracking catalyst and follow the mix reaction with a quench, using steam for example, the dehydrogenation catalyst can be located in a packed bed within a catalyst reactor 25 located downstream of the primary separation in separator 6. The paraffins formed by contact with the acidic catalyst will be dehydrogenated to their olefin counterpart.

20 Claims

1. A process for catalytically cracking a hydrocarbon feedstock to selectively produce C₃ to C₅ olefins, comprising the steps of:

- (a) introducing the hydrocarbon feedstock to a cracking reactor;
 - 25 (b) simultaneously delivering hot very high activity acid cracking catalyst solids to the cracking reactor;
 - (c) catalytically and thermally cracking the hydrocarbon feedstock with heat supplied by the hot, very high activity acidic catalyst solids to form a cracked product;
 - (d) separating the cracked product from the hot catalyst solids, and
 - 30 (e) quenching the separated cracked product,
- characterized in that the total kinetic residence time of the hydrocarbon feedstock from step (a) to step (e) is of from 0,05 s to 2,0 s, the temperature of the cracking reaction is of from 482 °C to 815 °C, the pressure of the cracking reactor is of from 0,69 bar to 6,9 bar (10 psi to 100 psi), the weight ratio of the catalyst solids to the hydrocarbon feedstock is of from 1:1 to 60:1, and the very
- 35 high activity acidic cracking catalyst is a zeolitic catalyst associated with a dehydrogenation catalyst consisting of a metal oxide selected from the oxides of iron, chromium, tin, or platinum on an inert carrier.

2. Process according to Claim 1, wherein the residence time is of from 0,05 s to 0,5 s.

- 40 3. Process according to Claim 1, further comprising the steps of:

- (f) delivering the separated catalyst solids to a stripper to remove the residual cracked gas products;
- (g) combusting the separated catalyst solids to remove carbon deposits and to heat the stripped catalyst solids to form regenerated catalyst solids, and
- 45 (h) transporting the regenerated catalyst solids to the cracking reactor.

4. Process according to Claim 1, wherein the temperature of the catalytic cracking reaction is from 537 °C (1000 °F) to 704,4 °C (1300 °F) and the residence time is from 0,1 s to 0,3 s.

- 50 5. Process according to Claim 1, wherein the hydrocarbon feedstock is selected from C₄ - C₇ paraffins, naphthas and light gas oils.

6. Process according to Claim 1, wherein the very high activity acidic catalyst is a catalyst support selected from the group consisting of silica gel, alumina and clay.

- 55 7. Process according to Claim 1, wherein the very high activity acidic catalyst is a catalyst selected from the group of zeolitic fluidized catalytic cracking catalysts, high activity ZSM-5, and rare-earth zeolites.

8. Process according to Claim 1, wherein the support for the dehydrogenation catalyst is selected from silica gel, silica-alumina, clays, or mixtures of any of the foregoing.
9. Process according to Claim 1, wherein the hydrocarbon feed stream and hot catalyst solids are delivered to a tubular thermal regenerative cracking reactor through a reactor feeder having vertical passages communicating with the tubular regenerative cracking reactor and the solids in a hot solids vessel, localized fluidization of the solids above the vertical passages is provided, and the hydrocarbon feed is delivered to the tubular thermal regenerative reactor at an angle to the path of the catalyst solids entering the tubular thermal regenerative reactor.
10. Process according to Claim 1, wherein the hot catalyst solids and the cracked product gases to be separated enter a separator through a separator inlet and reverse their direction 90°, whereafter the product gases reverse direction another 90° to effect a 180° reversal in direction relative to the entry direction, whereafter the catalyst solids continue in the path oriented 90° from the separator inlet and finally the path of the catalyst solids is directed downwardly and the separated product gases are quenched.
11. Process according to Claim 1, wherein the catalyst solids and cracked gases are separated in a separator comprising a chamber for rapidly disengaging 80% of the catalyst solids from the incoming mixed phase stream, said chamber having virtually rectilinear longitudinal side walls to form a flow path of height H and width W and a mixed phase inlet of inside width D_i , a gas outlet and a solids outlet, said inlet being at one end of the chamber and disposed normal to the flow path of height H which is equal to at least D_i , or 10, 2 cm (4 inches), whichever is the greater, the width W being from 0.75 D_i to 1.25 D_i , said solids outlet being at the opposite end of the chamber and suitably arranged for downflow of discharged solids by gravity, said gas outlet being therebetween at a distance no greater than 4 D_i from the inlet as measured between respective centerlines and oriented to effect a 180° change in the direction of the gas, whereby resultant centrifugal forces direct the catalyst solids in the incoming stream toward a wall of the chamber opposite to the inlet forming thereat and maintaining a virtually static bed of solids, the surface of the bed defining a curvilinear path of an arc of 90° of a circle for the outflow of solids to the solids outlet.

Patentansprüche

1. Verfahren zum katalytischen Cracken eines Kohlenwasserstoff-Aufgabegutes unter selektiver Ausbildung von C_3 - C_5 -Olefinen, umfassend die Stufen:
 - (a) Einführen eines Kohlenwasserstoff-Aufgabegutes in einen Crackreaktor;
 - (b) gleichzeitige Zufuhr eines heissen, äusserst hochaktiven, sauren Crackkatalysator-Feststoffes in den Crackreaktor;
 - (c) katalytisches und thermisches Cracken des Kohlenwasserstoff-Aufgabegutes unter Zugabe von Wärme, die aus dem heissen, sehr hochaktiven, sauren Katalysator-Feststoff stammt und unter Ausbildung eines Crackproduktes
 - (d) Abtrennen des Crackproduktes von den heissen Katalysator-Feststoffen; und
 - (e) Abschrecken des abgetrennten, gecrackten Produktes, dadurch **gekennzeichnet**, dass die gesamte kinetische Verweilzeit des Kohlenwasserstoff-Aufgabegutes aus Stufe (a) bis Stufe (e) 0,05 bis 2,0 Sekunden beträgt, die Temperatur der Crackreaktion 482 bis 815°C beträgt, der Druck des Crackreaktors von 0,69 bis 6,9 bar (10 bis 100 psi) beträgt, das Gewichtsverhältnis der Katalysator-Feststoffe zu dem Kohlenwasserstoff-Aufgabegut 1:1 bis 60:1 beträgt, und der äusserst hochaktive, saure Crack-Katalysator ein zeolithischer Katalysator ist, im Verbund mit einem Dehydrogenierungskatalysator, bestehend aus einem Metalloxid, ausgewählt aus Oxiden von Eisen, Chrom, Zinn oder Platin, auf einem inerten Träger.
2. Verfahren gemäss Anspruch 1, bei dem die Verweilzeit 0,05 bis 0,5 Sekunden beträgt.
3. Verfahren gemäss Anspruch 1, umfassend die weiteren Stufen
 - (f) Zuführen der abgetrennten Katalysator-Feststoffe zu einem Abstreifer zum Entfernen von restlichen Crackgasprodukten;
 - (g) Verbrennen der abgetrennten Katalysator-Feststoffe zum Entfernen von Kohlenstoffabscheidungen und zum Erhitzen der abgestreiften Katalysator-Feststoffe unter Ausbildung von regene-

rierten Katalysator – Feststoffen; und

(h) Transportieren der regenerierten Katalysator – Feststoffe zu dem Crackreaktor.

4. Verfahren gemäss Anspruch 1, bei dem die Temperatur der katalytischen Crackreaktion 537 ° C (1000 ° F) bis 704,4 ° C (1300 ° F) beträgt und die Verweilzeit 0,1 bis 0,3 Sekunden ist.
5. Verfahren gemäss Anspruch 1, bei dem das Kohlenwasserstoff – Aufgabegut ausgewählt ist aus C₄ – C₇ – Paraffinen, Naphthas und Leichtgasölen.
6. Verfahren gemäss Anspruch 1, bei dem der sehr hochaktive saure Katalysator ein Katalysatorträger ist, ausgewählt aus der Gruppe, bestehend aus Kieselgel, Aluminiumoxid und Ton.
7. Verfahren gemäss Anspruch 1, bei dem der sehr hochaktive saure Katalysator ein Katalysator ist, ausgewählt aus der Gruppe von zeolithischen fluidisierten katalytischen Crackkatalysatoren, hochaktivem ZSM – 5 und seltenen Erdzeolithen.
8. Verfahren gemäss Anspruch 1, bei dem der Träger für den Dehydrogenierungskatalysator ausgewählt ist aus Kieselgel, Siliciumdioxid – Aluminiumoxid, Tonen oder Mischungen aus den vorgenannten.
9. Verfahren gemäss Anspruch 1, bei dem der zugeführte Kohlenwasserstoffstrom und heisse Katalysator – Feststoffe in einen rohrförmigen Wärmeregenerierungs – Crackreaktor durch eine Reaktorzufuhr mit einer vertikalen Passage, die mit dem rohrförmigen Regenerierungs – Crackreaktor und den Feststoffen in einem heissen Feststoffkessel verbunden sind, zugeführt werden, eine lokalisierte Fluidisierung der Feststoffe oberhalb der vertikalen Passage vorgesehen ist, und der zugeführte Kohlenwasserstoff den rohrförmigen Wärmeregenerierungsreaktor in einem Winkel zu dem Pfad der Katalysator – Feststoffe, die in den rohrförmigen Wärmeregenerierungsreaktor eintreten, zugeführt wird.
10. Verfahren gemäss Anspruch 1, bei dem die abzutrennenden heissen Katalysator – Feststoffe und das gecrackte Produktgas in einem Abscheider durch einen Abscheidereinlass eintreten und ihre Richtung um 90 ° verändern, worauf anschliessend die Produktgase ihre Richtung um weitere 90 ° unter Ausbildung einer 180 ° – Richtungsumkehr relativ zu der Eintrittsöffnung verändern, worauf anschliessend die Katalysator – Feststoffe in einem Pfad mit einem Winkel von 90 ° von dem Abtrennereinlass gerichtet sind, weitergeführt werden und schliesslich der Pfad der Katalysator – Feststoffe nach unten gerichtet wird, und die abgetrennten Produktgase abgeschreckt werden.
11. Verfahren gemäss Anspruch 1, bei dem die Katalysator – Feststoffe und das gecrackte Gas in einem Abtrenner getrennt werden, umfassend eine Kammer für ein schnelles Abtrennen von 80 % der Katalysator – Feststoffe von dem einströmenden Mischphasenstrom, wobei die Kammer im wesentlichen geradlinige Längsseitenwandungen hat, unter Ausbildung eines Fließpfades der Höhe (H) und der Breite (W), und einen Mischphaseneinlass, der Innenbreite (D_i), einen Gasauslass und einen Feststoffauslass, wobei der Auslass an einem Ende der Kammer ist und sich normal zu dem Fließpfad der Höhe (H) befindet, die wenigstens D_i gleich ist, oder 10,2 cm (4 inches) beträgt, was immer grösser ist, und die Breite (W) 0,75 D_i bis 1,25 D_i beträgt, wobei der Feststoffauslass am entgegengesetzten Ende der Kammer ist und in geeigneter Weise angeordnet ist, so dass die abgegebenen Feststoffe durch Schwerkraft nach unten strömen, wobei sich der Gasauslass dazwischen in einer Entfernung von nicht mehr als 4 D_i von dem Einlass befindet, gemessen zwischen den jeweiligen Mittellinien, und so orientiert sind, dass eine 180 ° – Veränderung in Richtung des Gasstroms bewirkt wird, wodurch die sich ergebenden Zentrifugalkräfte die Katalysator – Feststoffe in dem einkommenden Strom gegen die Wand der Kammer gegenüber dem Einlass richten und ein im wesentlichen statisches Feststoffbett aufrecht erhalten, wobei die Oberfläche des Bettes einen kurvenförmigen Pfad mit einem Bogen von 90 ° eines Kreises für den Ausstrom der Feststoffe zu dem Feststoffauslass darstellt.

Revendications

1. Procédé de craquage catalytique d'une charge d'hydrocarbures, pour la production sélective d'oléfines en C₃ à C₅, comprenant les étapes consistant à :
 - (a) introduire la charge d'hydrocarbures dans un réacteur de craquage.

(b) introduire simultanément des produits solides chauds, constitués de catalyseur de craquage acide, à activité très élevée, dans le réacteur de craquage,

(c) effectuer le craquage catalytique et thermique de la charge d'hydrocarbures, grâce à la chaleur fournie par les produits solides chauds, constitués de catalyseur acide à activité très élevée, pour former un produit craqué,

(d) séparer le produit craqué des produits solides chauds, constitués de catalyseur, et

(e) tremper le produit craqué séparé,

caractérisé en ce que le temps de séjour cinétique total de la charge d'hydrocarbures, depuis l'étape (a) jusqu'à l'étape (e), est de 0,05 s à 2,0 s, la température de la réaction de craquage est de 482 °C à 815 °C, la pression du réacteur de craquage est de 0,89 bar à 6,9 bars (10 psi à 100 psi), le rapport en poids des produits solides constitués de catalyseur à la charge d'hydrocarbures est de 1:1 à 60:1, et le catalyseur de craquage acide, à activité très élevée, est un catalyseur zéolithique, associé à un catalyseur de déshydrogénation, constitué d'un oxyde métallique choisi parmi les oxydes de fer, de chrome, d'étain et de platine, fixé sur un support inerte.

2. Procédé selon la revendication 1, dans lequel le temps de séjour est de 0,05 s à 0,5 s.

3. Procédé selon la revendication 1, comprenant en outre les étapes consistant à :

(f) introduire les produits solides constitués de catalyseur, séparés, dans un purificateur, pour éliminer les produits gazeux craqués résiduels,

(g) effectuer la combustion des produits solides constitués de catalyseur, séparés, pour éliminer des dépôts de carbone et chauffer les produits solides constitués de catalyseur, purifiés, afin de former des produits solides constitués de catalyseur, régénérés, et

(h) amener les produits solides constitués de catalyseur, régénérés, au réacteur de craquage.

4. Procédé selon la revendication 1, dans lequel la température de la réaction de craquage catalytique est de 537 °C (1000 °F) à 704,4 °C (1300 °F) et le temps de séjour est de 0,1 s à 0,3 s.

5. Procédé selon la revendication 1, dans lequel la charge d'hydrocarbures est choisie parmi les paraffines en C₄ à C₇, les naphas et les gazoles légers.

6. Procédé selon la revendication 1, dans lequel le catalyseur acide à activité très élevée est un support de catalyseur, choisi parmi le gel de silice, l'alumine et l'argile.

7. Procédé selon la revendication 1, dans lequel le catalyseur acide à activité très élevée est un catalyseur choisi parmi les catalyseurs de craquage catalytique, fluidisés, zéolithiques, la zéolithe ZSM-5 à activité élevée et les zéolithes de terres rares.

8. Procédé selon la revendication 1, dans lequel le support pour le catalyseur de déshydrogénation est choisi parmi le gel de silice, les mélanges silice-alumine, les argiles et les mélanges de n'importe lesquels des composés précédents.

9. Procédé selon la revendication 1, dans lequel le courant de charge d'hydrocarbures et les produits solides chauds, constitués de catalyseur, sont introduits dans un réacteur de craquage thermique régénérateur, tubulaire, par l'intermédiaire d'un dispositif d'alimentation de réacteur, présentant des passages verticaux communiquant avec le réacteur de craquage régénérateur, tubulaire, et avec les produits solides contenus dans un récipient à produits solides chauds, une fluidisation localisée des produits solides est assurée au-dessus des passages verticaux, et la charge d'hydrocarbures pénètre dans le réacteur thermique régénérateur, tubulaire, en faisant un angle avec le trajet des produits solides, constitués de catalyseur, entrant dans le réacteur thermique régénérateur, tubulaire.

10. Procédé selon la revendication 1, dans lequel les produits solides chauds, constitués de catalyseur, et les produits gazeux craqués à séparer, entrent dans un séparateur par une entrée de séparateur, subissent un changement de direction de 90°, après lequel les produits gazeux subissent un autre changement de direction de 90° pour effectuer un changement de direction de 180° par rapport à la direction d'entrée, les produits solides, constitués de catalyseur, poursuivant leur route dans la direction faisant un angle de 90° avec l'entrée du séparateur et le trajet des produits solides, constitués de catalyseur, étant finalement dirigé vers le bas, et les produits gazeux séparés sont trempés.

11. Procédé selon la revendication 1, dans lequel les produits solides, constitués de catalyseur, et les gaz craqués sont séparés dans un séparateur comprenant une chambre permettant d'ôter rapidement 80 % des produits solides, constitués de catalyseur, du courant entrant, constitué d'une phase mixte, ladite chambre ayant des parois latérales longitudinales pratiquement rectilignes, formant un chemin d'écoulement de hauteur H et de largeur W, et une entrée de phase mixte, de largeur intérieure D_i , une sortie de gaz et une sortie de produits solides, ladite entrée étant à une extrémité de la chambre et étant disposée perpendiculairement au chemin d'écoulement de hauteur H qui est égale à au moins D_i ou à 10,2 cm (4 pouces), selon celle de ces valeurs qui est la plus grande, la largeur W étant de $0,75 D_i$ à $1,25 D_i$, ladite sortie de produits solides étant à l'extrémité opposée de la chambre et disposée de façon à permettre un écoulement vers le bas, par gravité, des produits solides évacués, ladite sortie de gaz étant située entre les deux, à une distance de l'entrée ne dépassant pas $4 D_i$, ladite distance étant mesurée entre les axes respectifs, et étant orientée de façon à réaliser un changement de 180° de la direction du gaz, ce qui fait que les forces centrifuges résultantes dirigent les produits solides, constitués de catalyseur, présents dans le courant entrant, vers une paroi de la chambre, opposée à l'entrée, où ils forment et maintiennent un lit, pratiquement statique, de produits solides, la surface du lit définissant un chemin curviligne correspondant à un arc de cercle de 90° , pour l'écoulement des produits solides vers la sortie de produits solides.

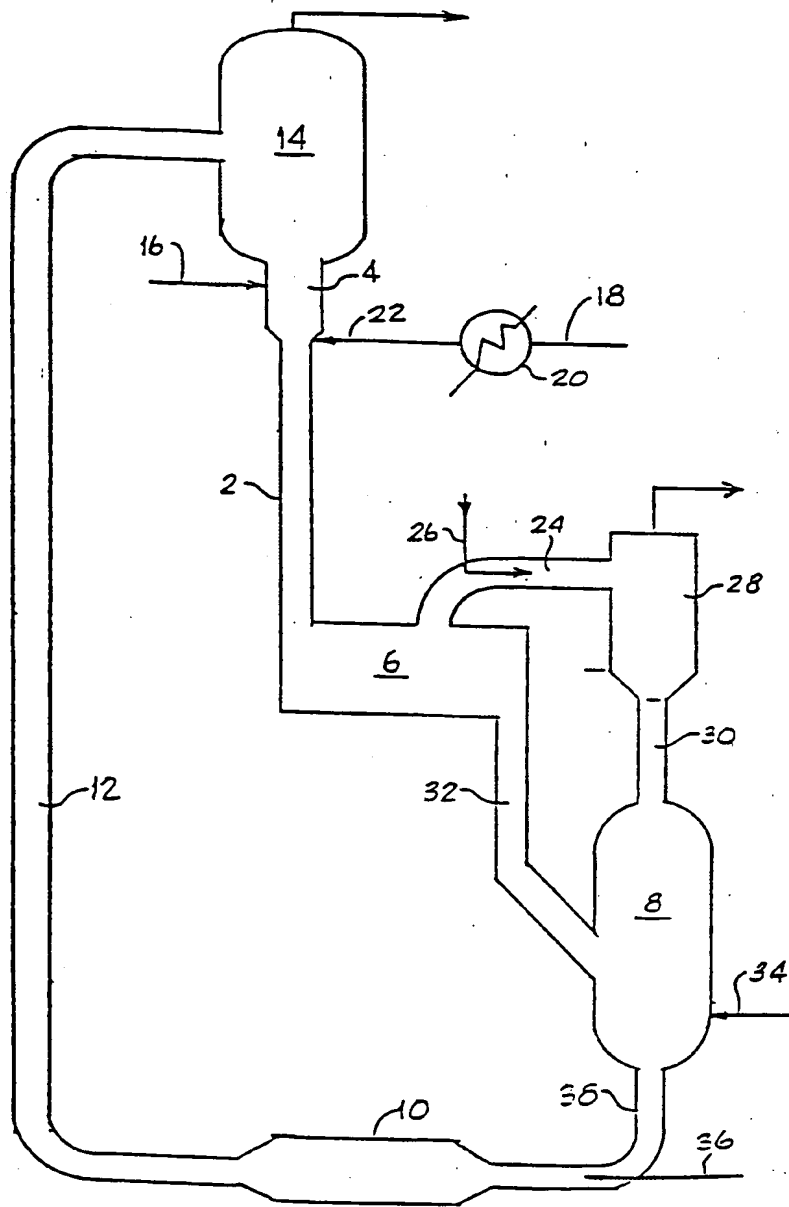
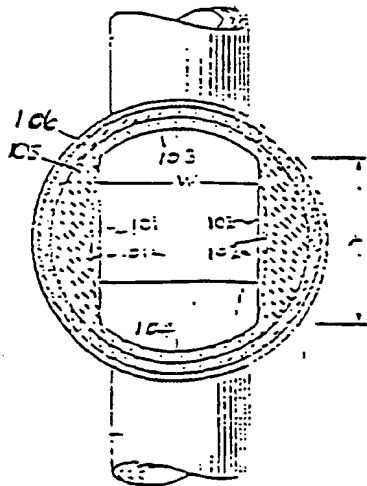
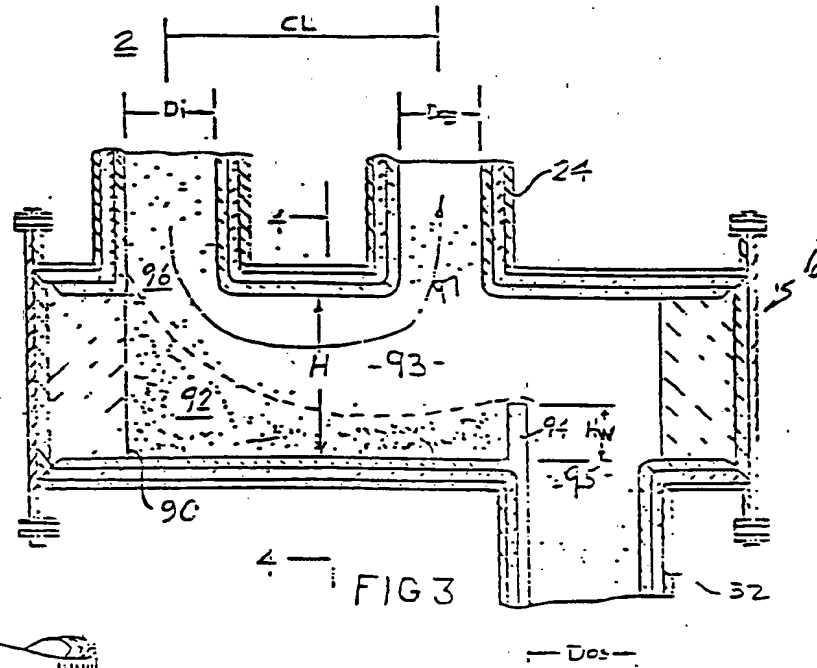


FIG.1



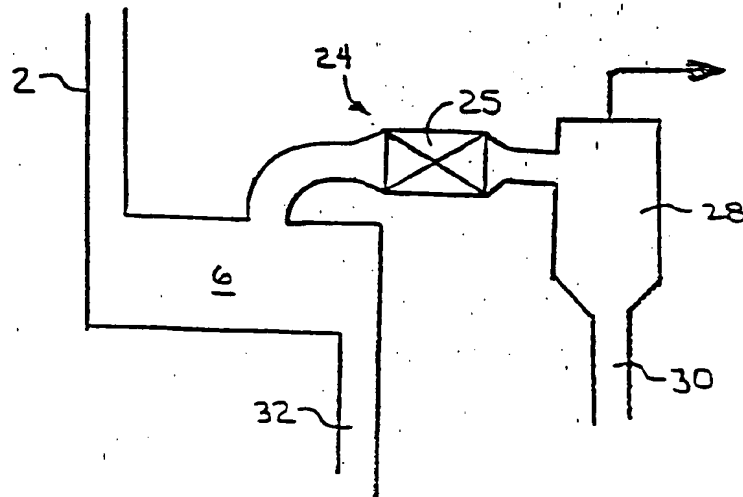


FIG 5

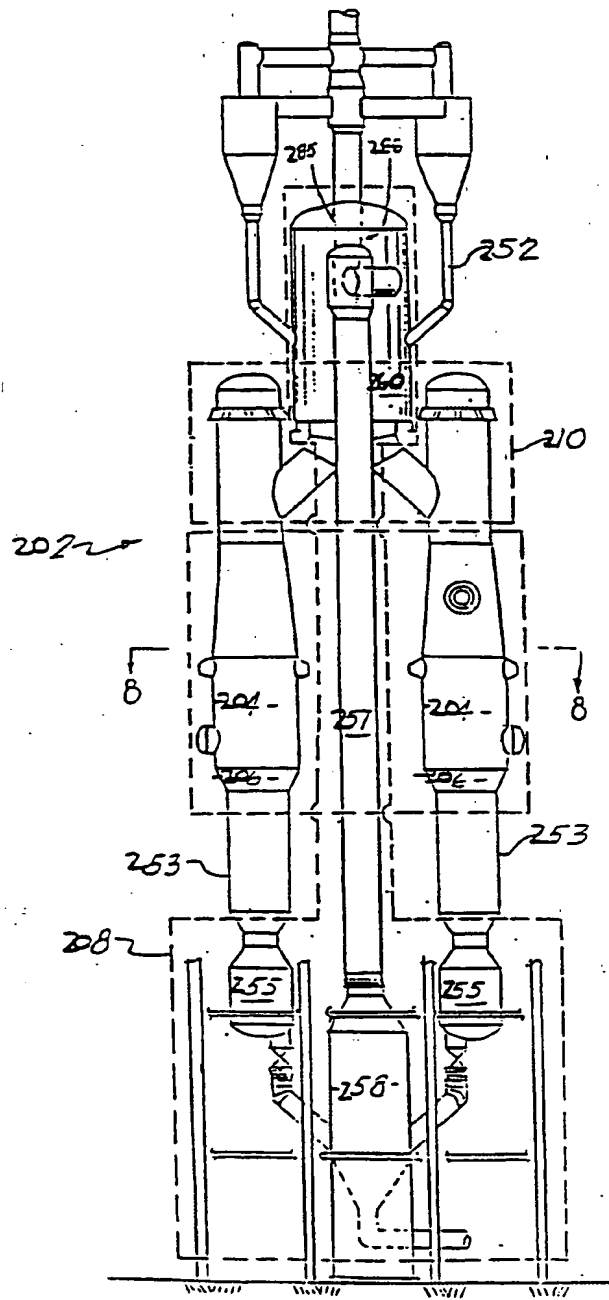


FIG 6

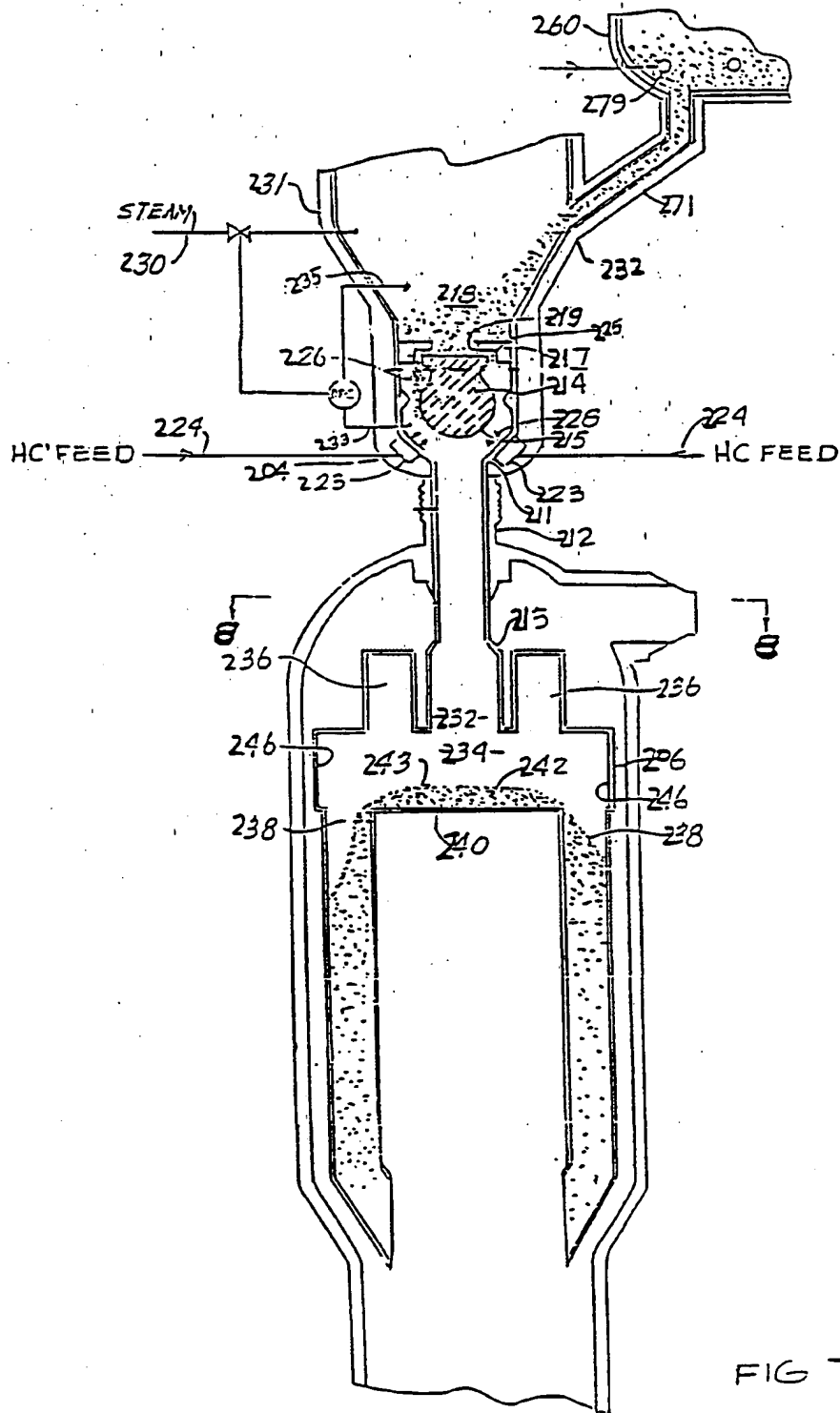


FIG 7

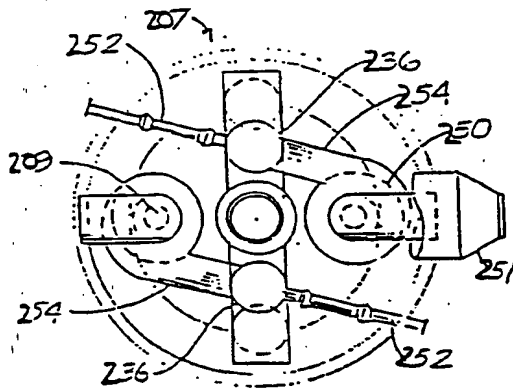


FIG. 8

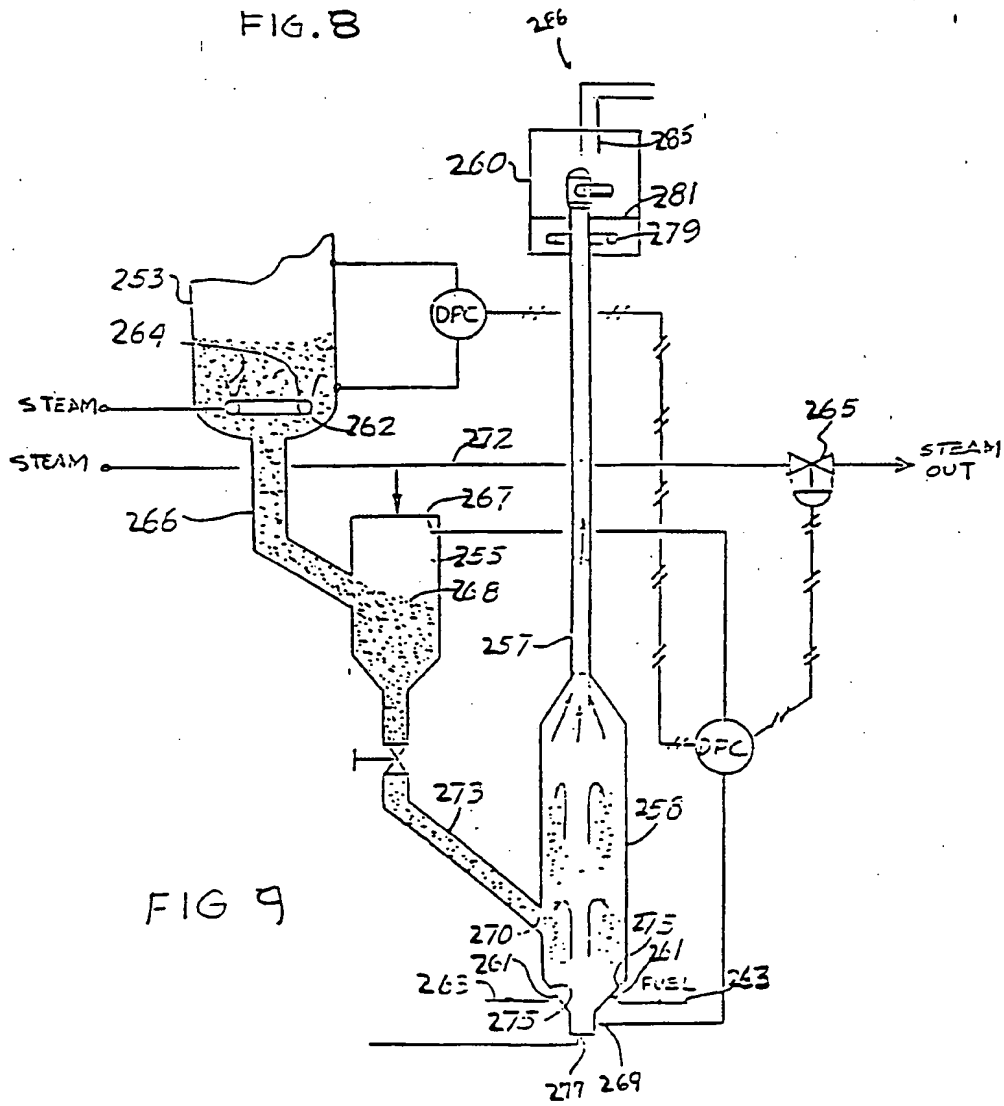


FIG 9